

# Stannum film electrode for square wave voltammetric determination of trace copper(II)

Yun Qing Tian · Hong Qun Luo · Nian Bing Li

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**Abstract** An anodic stripping voltammetric procedure for the determination of Cu(II) at an in situ-plated stannum film electrode (SnFE) was described. The results indicated that the SnFE had an attractive electroanalytical performance, with two distinct voltammetric stripping signals for copper and stannum, and showed the superior advantage for the determination of copper compared with the bismuth film electrode. Several experimental parameters were optimized. The SnFE exhibited highly linear behavior in the concentration range from 1.0 to 100.0  $\mu\text{g L}^{-1}$  of Cu(II) ( $r=0.994$ ) with the detection limit of 0.61  $\mu\text{g L}^{-1}$  ( $S/N=3$ ), and the relative standard deviation for a solution containing 40.0  $\mu\text{g L}^{-1}$  Cu(II) was 2.2% ( $n=8$ ). The procedure has been successfully applied for the determination of Cu(II) in lake water sample.

**Keywords** Stannum film electrode · Copper(II) · Anodic stripping voltammetry

## Introduction

Copper is an essential element that is used in a variety of industrial materials and is also an important micronutrient present in all living organisms. Although copper is needed by many living organisms at only very low levels to maintain carbohydrate and lipid metabolism, it is toxic when taken in excess. The concentration of copper in

waters and plants has resulted from industrial and domestic waste discharge, refineries, disposal of mining washing, and the use of copper compound as herbicide [1]. Therefore, the accurate determination of copper in the environmental samples is necessary. There are several techniques, which have been used for the determination of copper at low concentrations, such as electrothermal atomic absorption spectrometry [2], flame [3] and graphite furnace [4], atomic absorption spectrometry [5], chemiluminescence [6], inductively coupled plasma-mass spectrometry [7], and electrochemical methods [8–19]. Electrochemical methods, by right of the advantages of simple operation, inexpensive cost, and low detection limit, have revealed widest future in the determination of trace heavy metals including the determination of copper [8–19].

Bismuth film electrode (BiFE) has recently been used as a promising material for electrochemical analytical replacing mercury electrode with the advantages of its comparable characteristic, very low toxicity, and insensitivity to dissolved oxygen. Most of the earlier works on BiFE were to analyze metal ions such as Pb, Zn, Cd, Fe, Al, Tl, Sn, Co, and Mo as well as a few organic compounds like methyl parathion, metallothionein, thiamethoxam, and others [20–24]. However, the determination of copper using BiFE was difficult due to the similar stripping potentials of copper and bismuth, and a serious overlapping in bismuth and copper stripping signals limited the analysis [25, 26]. In order to resolve this problem, some methods have been reported. Wang et al. demonstrated that even though the standard potential of copper is higher than that of bismuth, the analysis of copper was feasible using bismuth film electrode. However, as the Cu(II) concentration was increased, the magnitude of the Bi(III) stripping pulse decreased, indicating competition between these two species for the electrode substrate (glassy carbon). Such

Y. Q. Tian · H. Q. Luo · N. B. Li (✉)  
Key Laboratory of Eco-environments in Three Gorges Reservoir  
Region (Ministry of Education), School of Chemistry  
and Chemical Engineering, Southwest University,  
Chongqing 400715, People's Republic of China  
e-mail: linb@swu.edu.cn

process caused double peaking for Cu(II) (one peak from the film and the other from the glassy carbon substrate) and calibration of copper at lower concentrations was difficult [27]. Prior et al. reported the use of gallium for improved determination of copper using the bismuth film electrode. The presence of gallium alleviated the problems of overlapping stripping signals usually observed between copper and bismuth when using the bismuth film electrode [28]. Aucélio et al. searched a new way to allow the sensitive determination of Cu(II) using the BiFE. The addition of hydrogen peroxide to the electroanalytical cell allowed the interference-free determination of Cu(II) using the BiFE. The  $\text{H}_2\text{O}_2$  has promoted a significant shifting of the Cu redissolution peak to a more positive potential and eliminated the competition with Bi(III) for glassy-carbon sites [29].

Stannum is a more “environmentally friendly” material and widely used in the food packaging industry. Recently, our laboratory has reported that a new electrode, stannum film electrode (SnFE), can be used for in situ determination of some heavy metals [30, 31]. Further experimental results showed that the stripping signals of stannum and copper did not overlap with each other. Therefore, in this paper, we provided a new method for analysis of copper at the SnFE without adding masking agent. The SnFE has revealed the advantages on the determination of copper compared with the BiFE. This new electrode has been applied to the analysis of Cu(II) in lake water sample with satisfactory results.

## Experimental

### Reagents

All chemicals employed in this work were of analytical reagent grade. Cu(II) was prepared by diluting the standard stock solution prepared with  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Stock solution of stannum ( $100.0 \text{ mg L}^{-1}$ ) was prepared by dissolving  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  with  $0.2 \text{ mol L}^{-1}$  HCl. Glacial acetic acid and sodium acetate were obtained from Dachuan Fine Chemical Co., Ltd. (Ningbo, China). Doubly distilled water was used in the preparation of solutions throughout this study. Lake water sample was taken from a lake in Southwest University.

### Apparatus

All the electrochemical experiments were performed with a CHI 660B electrochemical station (CHI Instrument Co., USA). A three-electrode system was used for the voltammetric measurements, which comprised a platinum auxiliary electrode, an Ag/AgCl reference electrode and a glassy carbon working electrode with diameter of 3 mm. A pHs-3D pH meter (Shanghai Analytical Instrument Factory, Shanghai, China) was used for pH measurement.

All experiments were carried out in a 10 mL electrochemical cell.

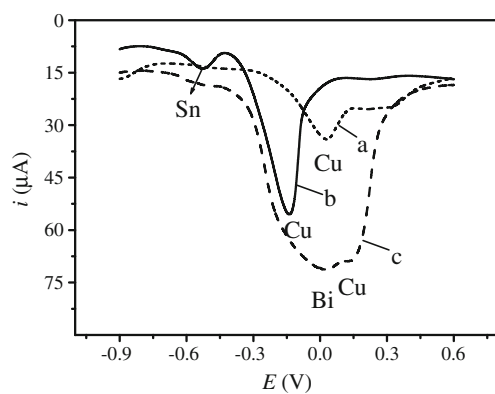
### Procedures

Before use, the glassy carbon electrode (GCE) was polished with water slurry of  $0.05 \mu\text{m}$  alumina powder on a polishing cloth to a shiny surface. Then, the electrode was rinsed with 1:1  $\text{HNO}_3$ , absolute ethanol, and distilled water, respectively, in an ultrasonic bath to remove residual polishing material. In situ stannum film deposition was carried out by adding stannum ion and copper ion to 3.0 mL of  $0.1 \text{ mol L}^{-1}$  acetate buffer (pH 4.0) simultaneously. A preconcentration potential of  $-1.50 \text{ V}$  was applied to the working electrode under stirred conditions. After an equilibration time of 10 s, the square wave anodic stripping voltammograms were recorded between  $-1.00$  and  $0.60 \text{ V}$  with a frequency of 35 Hz, amplitude of 75 mV, and step increment of 5 mV. Prior to the next process, the electrode was cleaned by holding the potential at  $0.40 \text{ V}$  for 30 s under stirred conditions. All experiments were done at room temperature.

## Results and discussion

Square wave voltammetric response of Cu(II) at the SnFE

Differential pulse anodic stripping voltammetry and square wave voltammetry (SWV) were compared for the determination of copper under identical conditions. The higher peak, flatter baseline, and favorable reproducibility were obtained by using SWV. Therefore, SWV was selected for subsequent experiments. Figure 1 shows the square wave voltammograms of  $100.0 \mu\text{g L}^{-1}$  Cu(II) at the bare GCE (curve a), the stannum film electrode (curve b), and the bismuth film electrode (curve c). It can be seen from Fig. 1 that the SnFE exhibited a well-defined and acuminous signal for copper compared with the GCE. The oxidation peaks of copper and stannum can be seen at  $-0.14$  and  $-0.53 \text{ V}$ , respectively. The two stripping peaks have been separated distinctly without any overlapping. However, the obvious peak overlapping between copper and bismuth can be seen from curve c in Fig. 1. Therefore, the SnFE reveals the advantages on the determination of copper compared with the BiFE. In comparison with the bare GCE, the peak potential of copper at the SnFE shifted to a negative potential more than  $0.1 \text{ V}$ . The reason for the shift may attribute to the formation of intermetallic compounds between stannum and copper. The formation of intermetallic compounds between metals, which have been co-deposited onto the electrode surface, is a common phenomenon in stripping voltammetric measurements [20].



**Fig. 1** Square wave anodic stripping voltammograms of Cu(II) at the glassy carbon electrode (**a**), the stannum film electrode (**b**), and the bismuth film electrode (**c**) in 0.1 mol L<sup>-1</sup> acetate buffer (pH 4.0). **a** 100.0 μg L<sup>-1</sup> Cu(II), **b** 100.0 μg L<sup>-1</sup> Cu(II) and 10.0 mg L<sup>-1</sup> Sn (II), **c** 100.0 μg L<sup>-1</sup> Cu(II) and 1.0 mg L<sup>-1</sup> Bi(III). Deposition potential, -1.50 V; deposition time, 210 s; frequency, 35 Hz; amplitude, 75 mV; step increment, 5 mV

Copper and stannum were likely to form intermetallic compounds such as Cu<sub>6</sub>Sn<sub>5</sub> and Cu<sub>3</sub>Sn [32], which caused the negative shift of peak potential. However, the negative shift of peak potential at the SnFE almost has no influence on the peak separation of copper and stannum (as shown in curve b of Fig. 1).

#### Effects of SWV parameters

The effects of frequency and amplitude on the signal of copper were studied to confirm the optimum waveform for the analysis of copper. The two parameters were investigated in 0.1 mol L<sup>-1</sup> acetate buffer (pH 4.0) containing 100.0 μg L<sup>-1</sup> Cu(II) and 6.0 mg L<sup>-1</sup> Sn(II). The square wave frequency had a significant effect on the stripping response of copper. The increase of frequency up to 35 Hz caused the signal of copper to increase steadily; over this frequency, the stripping response decreased. The square wave amplitude was investigated in the range from 10 to 100 mV. When the amplitude increased, the stripping response gradually increased. However, the peak position shifted to the cathode direction with the increase of amplitude, which is unfavorable to the signal separation of copper and stannum. Therefore, the frequency of 35 Hz and the amplitude of 75 mV were chosen for the following SWV experiments.

#### Effect of pH

The effect of the pH value of the acetate buffer on the peak current of copper was investigated and the results indicated the voltammetric response increased slowly between 3.5 and 4.0, followed by a sharp decrease between 4.0 and 5.5. The highest peak current of Cu(II) was obtained at pH 4.0.

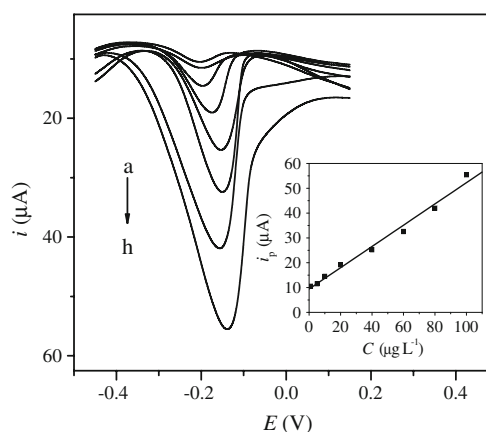
The sharp decrease of peak current may ascribe to the hydrolysis of stannum and copper with an increase in pH. For a high sensitivity of the SnFE, pH 4.0 was selected in the following work.

#### Effect of the stannum concentration

The effect of different concentrations of Sn(II) on the peak current of copper in 0.1 mol L<sup>-1</sup> acetate buffer containing 100.0 μg L<sup>-1</sup> Cu(II) was studied and the results showed that the stripping peak current of copper steadily increased as the concentration of Sn(II) up to 10.0 mg L<sup>-1</sup>, and then dramatically decreased. Consequently, a stannum concentration of 10.0 mg L<sup>-1</sup> was used in subsequent work. Under optimum conditions including a stannum concentration of 10.0 mg L<sup>-1</sup>, the stannum film electrode exhibited highly linear behavior in the concentration range from 1.0 to 100.0 μg L<sup>-1</sup> of Cu(II).

#### Effects of the deposition time and deposition potential

To improve the electroanalytical performance of the in situ-plated stannum electrode, the preconcentration parameters including the deposition time and deposition potential should be optimized. The effect of the deposition time was studied in the range of 30–270 s for 0.1 mol L<sup>-1</sup> acetate buffer containing 100.0 μg L<sup>-1</sup> Cu(II) and 10.0 mg L<sup>-1</sup> Sn (II). The peak current increases linearly with the deposition time up to 150 s. Over the deposition time of 150 s, the peak current deviates from linearity because of the gradually



**Fig. 2** A series of voltammograms for 1.0–100.0 μg L<sup>-1</sup> of Cu(II) on the in-situ plated stannum film electrode. Supporting electrolyte: 0.1 mol L<sup>-1</sup> acetate buffer (pH 4.0) and 10.0 mg L<sup>-1</sup> Sn(II). Concentrations of Cu(II): **a** 1.0 μg L<sup>-1</sup>, **b** 5.0 μg L<sup>-1</sup>, **c** 10.0 μg L<sup>-1</sup>, **d** 20.0 μg L<sup>-1</sup>, **e** 40.0 μg L<sup>-1</sup>, **f** 60.0 μg L<sup>-1</sup>, **g** 80.0 μg L<sup>-1</sup>, **h** 100.0 μg L<sup>-1</sup>. Deposition potential, -1.50 V; deposition time, 210 s; frequency, 35 Hz; amplitude, 75 mV; and step height, 5 mV. A 30-s cleaning step at 0.40 V was applied to the electrode between measurements. *Inset* the calibration curve of Cu(II) at the stannum film electrode with SWV

**Table 1** Comparison of this method for the determination of Cu(II) with other electrochemical methods

| Electrode substrate   | Method                             | Linear range (M)                            | LOD (M)                                       | Ref.                 |           |
|---|------------------------------------|---|---|----------------------|-----------|
| 3MT/3TA copolymer/Au  | SWV                                | $1.0 \times 10^{-7}$ – $1.0 \times 10^{-6}$ | $6.0 \times 10^{-8}$                          | [8]                  |           |
| 4-Carboxyphenyl-grafted SPEs  | SWV                                | $7.5 \times 10^{-9}$ – $1.8 \times 10^{-7}$ | $5.0 \times 10^{-9}$                          | [9]                  |           |
| Cysteine modified mercury film  | LSV                                | $1.0 \times 10^{-9}$ – $1.0 \times 10^{-5}$ | $5.0 \times 10^{-10}$                         | [10]                 |           |
| 3MT 3-methyl thiophene, 3TA 3-thiophene acetic acid, SPEs screen-printed electrodes, BHAB Bis(2-hydroxyacetophenone) Butane-2,3-dihydrazone, Poly L poly(ethylenediamine tetra-N-(3-pyrrole-1-yl)-propylacetamide), SWV square wave voltammetry, LSV linear sweep voltammetry, CV cyclic voltammetry, DPV Differential pulse voltammetry, PGPT potentiometric generic pulse technique | Poly(pyrrole-malonic acid)/GCE     | SWV   | $1.0 \times 10^{-7}$ – $5.0 \times 10^{-6}$   | $5.0 \times 10^{-8}$ | [11]      |
|   | BHAB/carbon paste electrode        | LSV   | $1.0 \times 10^{-7}$ – $2.0 \times 10^{-5}$   | $8.3 \times 10^{-8}$ | [12]      |
|   | Poly L/GCE                         | DPV   | $5.0 \times 10^{-8}$ – $1.0 \times 10^{-5}$   | $5.0 \times 10^{-8}$ | [13]      |
|   | Poly-4-nitroaniline/GCE            | PGPT  | $5.0 \times 10^{-13}$ – $5.0 \times 10^{-9}$  | –                    | [14]      |
|   | Mercury nano-droplets              | SWV   | –   | $1.2 \times 10^{-8}$ | [15]      |
|   | Gold disk microelectrode           | SWV   | $1.0 \times 10^{-6}$ – $1.0 \times 10^{-4}$   | $2.5 \times 10^{-6}$ | [16]      |
|   | 2,5-Dimercapto-1,3,4-thiadiazol/Au | LSV   | $8.5 \times 10^{-6}$ – $8.5 \times 10^{-5}$   | $4.0 \times 10^{-7}$ | [17]      |
|   | Penicillamine/Au                   | CV  | $8.0 \times 10^{-7}$ – $1.0 \times 10^{-4}$   | $4.0 \times 10^{-7}$ | [18]      |
|   | Graphite-based Hg-SPEs             | SWV   | $1.56 \times 10^{-8}$ – $1.56 \times 10^{-5}$ | $7.8 \times 10^{-9}$ | [19]      |
|   | Stannum film electrode             | SWV   | $1.56 \times 10^{-8}$ – $1.56 \times 10^{-6}$ | $9.5 \times 10^{-9}$ | This work |

saturated surface. The peak current of Cu(II) tends to be constant when the deposition time is above 210 s. The effect of the deposition potential was studied in the potential range of  $-0.60$  to  $-2.00$  V. The highest peak current of Cu(II) was obtained at the deposition potential of  $-1.50$  V. Therefore, the deposition time of 210 s and the deposition potential of  $-1.50$  V were chosen for further work.

#### Calibration data

A series of voltammograms for the concentration range from  $1.0$  to  $100.0 \mu\text{g L}^{-1}$  of Cu(II) are illustrated in Fig. 2, together with the relevant calibration curve of peak current against concentration of Cu(II). The linear regression equation of Cu(II) is  $i_p = 0.04281C + 0.94424$  ( $i_p$ ,  $10^{-5}$  A;  $C$ ,  $\mu\text{g L}^{-1}$ ) with the correlation coefficient of 0.994, and the detection limit is  $0.61 \mu\text{g L}^{-1}$ . The reproducibility of the SnFE has been evaluated and the relative standard deviation for eight successive measurements was 2.2% for Cu(II) in a solution of  $40 \mu\text{g L}^{-1}$  level. The electrochemical determination of Cu (II) has also been studied by other researchers. A number of different modified electrodes and different detection techniques were applied for this detection. We have compared the detection limits and other figure of merits by the use of different electrochemical methods for determination of copper ions and the results are shown in Table 1. It can be seen from Table 1 that the method proposed has relatively lower detection limit than those of some other electrochemical methods.

**Table 2** Results for the determination of Cu(II) in the samples

| Original ( $\mu\text{g L}^{-1}$ ) | Added ( $\mu\text{g L}^{-1}$ ) | Found <sup>a</sup> ( $\mu\text{g L}^{-1}$ ) | Recovery (%) |
|-----------------------------------|--------------------------------|---|--------------|
| 7.70                              | 10.00                          | 17.30                                       | 96.0         |
| 7.70                              | 20.00                          | 28.44                                       | 103.7        |
| 7.70                              | 30.00                          | 37.62                                       | 99.7         |
| 7.70                              | 40.00                          | 47.49                                       | 99.5         |

<sup>a</sup> Mean of three determinations

#### Interferences

The foreign substances were used to evaluate the selectivity for the determination of Cu(II) at the SnFE. The influences of the foreign substances on the determination of  $40.0 \mu\text{g L}^{-1}$  Cu(II) were performed. 50-fold of Cd(II), Pb (II), Al(III), Ni(II), and Co(II); 1,000-fold of K(I), Na(I),  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  did not interfere with the determination of Cu(II), whereas 50-fold of Zn(II) and Fe (III) produced interferences. The reason is probably due to the competition between interfering ions and copper for the surface sites, as well as the formation of intermetallic compounds between copper and other metal ions [20, 33].

#### Determination of Cu(II) in lake water sample

The practical analysis was tested using a real water sample obtained directly from a lake of Southwest University; 5.0 mL of water sample, 3.0 mL of  $0.1 \text{ mol L}^{-1}$  acetate buffer, and 1.0 mL of  $100.0 \text{ mg L}^{-1}$  Sn(II) were diluted to 10.0 mL and the determination was carried out as the procedure described above. The Cu(II) concentration determined in the lake water sample was  $7.70 \mu\text{g L}^{-1}$  ( $n=3$ ). The different concentrations of Cu(II) solutions were acquired by adding standard Cu(II) solutions of various concentrations in the lake water and the determination results are listed in Table 2, in which the total concentration of Cu (II) was obtained with the SnFE according to the above

experimental approach. The recoveries to sample solution of different concentrations were between 96.0% and 103.7%. The experimental results suggested that the SnFE had great potential for the practical sample analysis.

## Conclusions

This work reports the determination of trace Cu(II) by SWV on the nontoxic SnFE. Compared with the BiFE, the SnFE reveals special advantages in the determination of copper. Owing to the different stripping peak potentials, the SnFE exhibited well separated and distinct stripping peaks for both stannum and copper with a low background. The practical application of the SnFE was successfully performed by measurement of copper ion in the lake water sample.

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